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The role of SO_2 in the chemistry of amine-based CO_2 capture in PCC

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Abstract

Most coals contain a certain amount of sulfur. Upon combustion most of the sulfur is initially oxidized to SO_2 and later to SO_3 and sulfuric acid. If gaseous SO_2 enters the amine-based post combustion capture (PCC) plant it is immediately absorbed into the amine solution and transformed initially into sulfurous acid which dissociates into protons and the sulfite ion, SO_3^{2-}. The protons and sulfite remain in the amine solution and will accumulate over time. In this investigation we have studied the long term effect of dissolved SO_2 in MEA (monoethanolamine) solutions kept at 100°C by following the NMR spectrum of the solution. Additionally we have modeled the effect of increasing amounts of accumulated SO_2 on the cyclic capacity of the MEA solution as well as the reaction kinetics of dissolved CO_2.

Keywords: PCC; monoethanolamine; sulfur dioxide; cyclic capacity; kinetics

1. Introduction

The effects of the absorption of sulfur dioxide, SO_2, into amine solutions for PCC applications are at least potentially very complex. SO_2 can react with the amine to form the sulfurous acid amide and it will react with water to form sulfurous acid, H_2SO_3, which will dissociate releasing two protons and the sulfite ion, SO_3^{2-}. The sulfite ions will not play an important role (rather than formation of Heat Stable Amine Salts) but the released protons by lowering the pH will interfere in the equilibriums of the amine, hydroxide, and CO_2 in the formation of carbamate and carbonate species.

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The investigation includes two aspects: (a) the long term interactions of 0.1M S(IV) dissolved in a 0.05M solution of MEA at 40 and 100°C as measured by ^{1}H-NMR spectroscopy and (b) the modelling of the effects of accumulating SO_2 in the MEA solution with respect to CO_2 absorption equilibriums and kinetics.

2. Experimental

Analytical grade sodium sulfite, monoethanolamine, and hydrochloric acid were used as supplied without further purification. All solutions were prepared using ultra-pure Milli-Q water that had been boiled for one hour to remove dissolved CO_2 and O_2.
Equilibrium investigations of monoethanolamine and sulfite were conducted at 40 and 100°C. Several sample solutions of 2:1 Na_2SO_3:MEA were prepared. Different volumes of HCl were then added to the mixture of the solutions to cover the pH range from 10 to 3. All the samples were thermostatted in water and oil bath at 40 and 100°C, respectively.
In modelling of the reactions we have used the reported values in the literature [1-3] for the kinetic and equilibrium constants at 40 and 100°C. Speciation of the solution at top of the absorber has been calculated based on the equilibration of the solution at the bottom of the desorber (1:5 CO_2:MEA) before it is ready to be transferred to start the CO_2 absorption. The modelling was done for a range of added amounts of SO_2 from 0 to 1.5M.
The kinetics was modelled as the addition of 0.035M CO_2 to the equilibrated solutions at the top and at the bottom of the absorber column.

3. Results NMR investigation

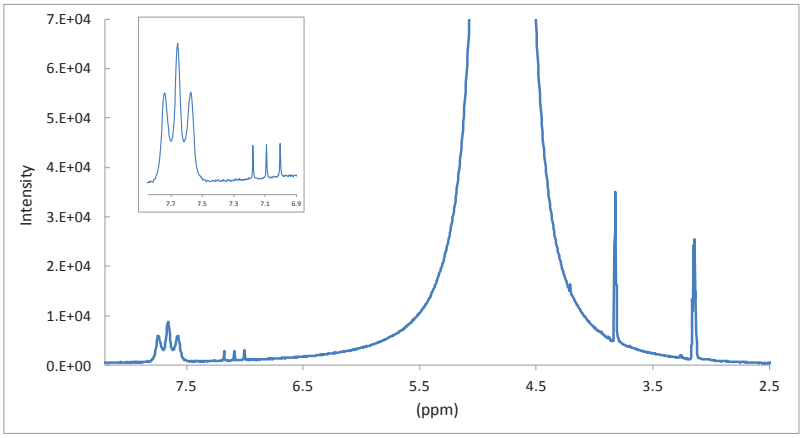

Figure 1. NMR spectra of 0.05M of MEA solution with 0.1M of sulfite at pH=7.2 equilibrated for five months at 100°C. Inset is an enlargement of the peaks of the produced ammonium and protonated nitrogen of the MEA

Degradation/reaction of MEA with SO_2

According to the reports in the literature[4-6] in a real PCC process the amine capacity for CO_2 capture is reduced by SO_2 as a result of irreversible reaction of amine with S(IV) species. Interaction of sulfur species with amine is slow and complex and not much detail is known. Qualitative ^{1}H-NMR spectroscopic studies of interactions of MEA with sulfur species at typical absorber temperature, 40°C, did not show any sign of interactions, formation of sulfurous acid amide the carbamate equivalent in the

CO_2 system, for a period of two weeks. Based on these results we have concluded that in aqueous solutions and under our experimental conditions SO_2 does not react with amines. It is possible that these types of reactions are very slow at low temperature and happen with faster kinetics at higher temperature of the desorber in PCC process. In order to investigate the occurrence of these reactions at high temperatures, similar experiments were conducted by equilibrating samples in pressure resistant NMR tubes at 100°C in an oil bath for more than nine months and recording their ^{1}H-NMR spectra regularly. Similar to low temperature, NMR spectroscopy results at high temperature do not show any interaction between S(IV) species and amine. However, at high temperature thermal degradation of MEA occurs as three singlets of ammonium ion start to appear with increasing in the intensity by time (approx. 7.1 ppm). The broad triplet at 7.7 ppm is assigned to the amine protons of MEA. There is also a slight shift of CH_2 peaks of MEA with time to higher ppm. The shift is the evidence of the protonation on the nitrogen atom. This can be as a result of oxidation of S(IV), sulfite, to S(VI), sulfate, in the presence of dissolved oxygen. Sulfuric acid is a stronger acid than sulfurous acid and oxidation will reduce the pH causing protonation of monoethanolamine.

It is worthwhile to mention that all the ^{1}H-NMR results from this investigation has been conducted in glass vessels and in absence of any metal which may play a significant role in catalysing reactions at real PCC conditions.

4. Results absorption modeling

Considering that there is no observable direct interaction between SO_2 and MEA, even at elevated temperature over several months, the remaining effect of accumulation of SO_2 into the MEA solution is the acid behaviour of the sulfurous acid. There are several effects of lowering of the pH. The immediate kinetic effects include: (a) protonation of MEA, reducing the concentration of free MEA that reacts with CO_2, thus reducing the kinetics of carbamate formation; (b) lowering the hydroxide concentration, thus reducing the kinetics of carbonate formation. The equilibrium effects are more subtle and complex but generally there is a reduction of the absorption capacity of the amine solution with increasing accumulation of SO_2.

We begin with the equilibrium analysis. Figure 2 (a) represents the total amount of absorbed CO_2 in the form of carbonates and carbamates as a function of accumulated SO_2 up to 1.5 M at the bottom of the absorber and desorber columns. At both positions in the PCC process the total amount of CO_2 decreases with increasing accumulated SO_2. The high loading decreases almost linearly while the affect at low loading is non-linear. More instructive is the dependence of the cyclic capacity of the amine solution, the amount of CO_2 separated per mole of amine, see Figure 2 (b). The cyclic capacity is about 1.5 moles of CO_2 per 5 moles of MEA for the 40°C to 100°C temperature cycle at zero SO_2. Initially, this capacity reduces with absorbed SO_2 only very marginally; the drop accelerates from about 0.5 M SO_2 to reach a minimum cyclic capacity of about 0.9 moles CO_2 per 5 moles of MEA, a reduction of 40%.

It is interesting to relate this final concentration to the number of cycles for different levels of SO_2 content in the flue gas. In Australia there is no flue gas desulfurization; at a relatively low level of SO_2 of 100 ppm 1500 cycles are required to reach 1.5 M SO_2. At the relatively high SO_2 contamination of 500 ppm, only 300 cycles are required. Flue gas desulfurization reduces the SO_2 content to about 75 ppm, then the high SO_2 content is reached after 2000 cycles.

While the reduction of the cyclic capacity of 40% for the highest calculated concentration of accumulated SO_2 is not acceptable in practice, it is encouraging to observe that the initial reduction is much smaller, about 5% up to 0.3 M SO_2.

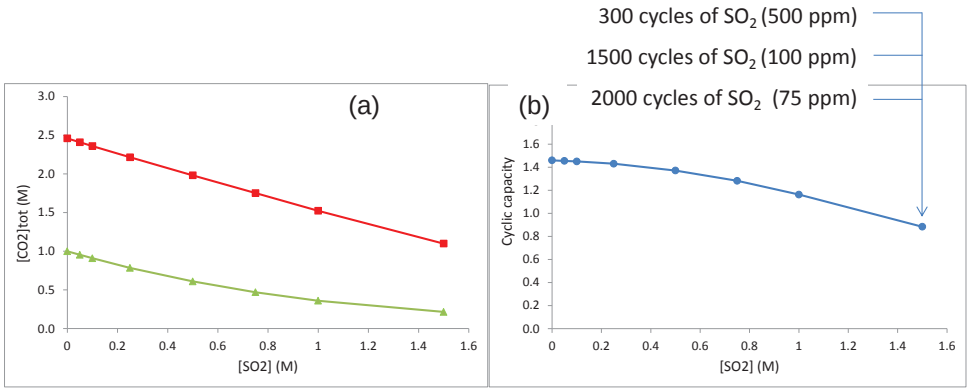

Figure 2. (a) Total CO_2 content of solutions with different amount of SO_2 present; bottom of the absorber (red line), and desorber (green line). (b) Simulated cyclic capacity, as moles of CO_2 per 5 moles of MEA, of CO_2 at different concentrations of SO_2 present in inlet flue gas (in the absence of thermal degradation).

The kinetics effects can easily be modelled in a batch mode, however, the modelling of an absorber or stripper column is presently out of our reach. In order to approximate the effect of accumulated SO_2 on the kinetics we model the kinetics of the reactions of CO_2 at the top of the absorber column and at the bottom. Figure 3 displays the kinetics of CO_2 transformation into carbonates and carbamates by adding 0.035 M CO_2 to the equilibrated solutions. At the top of the absorber column where the amine solution is very lean the kinetics is much faster than at the bottom where the solution is already CO_2 rich. Interestingly, the relative effects of the introduction of 1.5M SO_2 is much more pronounced for the lean solution with a slowing down of the process by approximately a factor of 2. For the rich solution the effect is significantly smaller.

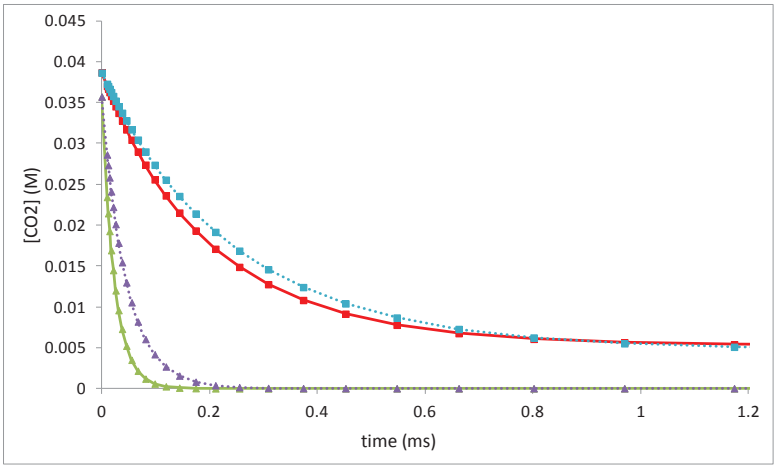

Figure 3. Kinetics of CO_2 absorption in aqueous MEA at top (triangles) and bottom (squares) of the absorber; solid lines in the absence and dashed lines in the presence of 1.5M SO_2.

In summary of equilibrium and kinetic effects of accumulated SO_2 is small up to a concentration of 0.3 M SO_2 with an effect hardly larger than 5%. If the concentration increases further both equilibrium and

kinetic effects start to be noticeable with a decrease of the cyclic capacity by 40% and a reduction of the CO_2 transformation kinetics by a factor of 2.

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